

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improved Papermaking Process

We, NALCO CHEMICAL COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 6216 West 66th Place, Chicago, State of Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates in general to an improved papermaking process, and more particularly to a method for increasing the rate at which water drains from pulp fiber in the formation of paper. In the process, a combination of an aluminum ion source such as alum, a cationic component, and an anionic polymer was found to increase markedly the rate at which water drains from the paper web without adversely affecting the properties of the paper.

The rate at which paper can be manufactured has been found to be directly related to the rate of water drainage from the aqueous suspension of paper fibers. A paper machine can produce paper only as fast as the wet may be removed from the machine. If the wet web is drawn off the machine at too great a speed, the web will break, resulting in a substantial loss of production time. While this problem is not too serious on tissue or other light grades of paper, it is especially important in the production of heavier paper or board having a basis weight in excess of 30 lbs./1000 ft.².

Substantial efforts have been expended by the papermaking art to increase this drainage rate and thereby more efficiently carry out the overall papermaking process. For example, it has been found that less refined pulp possesses greater wet web strength, and thus exhibits superior drainage properties, thereby

allowing the use of faster machine speeds. However, pulp which has not been refined to any substantial degree, produces paper which has unsatisfactory dry strength. Consequently, when the low refining technique is used to increase machine speed, the quality of the paper is poor and often is unacceptable.

To counteract the adverse effect on dry strength caused by using less refined pulp, attempts have been made to improve the paper by chemical means. In some instances, however, artificially produced strength is accompanied by unwanted side effects in the resulting paper such as brittleness or poor resistance to fold and/or crease stresses. Further, the use of dry strength treatments has on occasion adversely affected the drainage rate, thereby reducing the speed at which paper may be produced. Another factor which complicates paper manufacturing is the use of various fillers, pigments, sizing additives and the like, which use often adversely affects the drainage rate.

It would be of great advantage to the papermaking art if a process could be derived which would substantially increase the rate of drainage of water from aqueous suspensions of paper fibers. Such a process would allow greater machine speed and, further, would permit the paper manufacturer to increase the amount of pulp refining so that paper of higher quality could be produced.

Accordingly, it is an object of this invention to provide a process wherein the drainage rate of water from an aqueous suspension of paper pulp fibers is materially increased.

It is a further object of this invention to provide a process whereby pulp may be more highly refined prior to its use in a paper-making process without bringing about unwanted secondary effects such as loss of wet strength and decreased drainage rates.

[Price

It has now been discovered that the overall operational efficiency of the papermaking process may be materially improved by the process of this invention. Specifically, the process of this invention comprises the sequential addition of a cationic component comprising an aluminum ion source and a material selected from cationic polymers, cationic starches and cationic gums, followed by the addition of an anionic high molecular weight polymer to the aqueous suspension of paper pulp prior to its formation into paper. In a preferred embodiment of the invention specific cationic materials and anionic polymers are employed for this purpose.

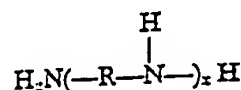
The first component used in the process of this invention comprises a dual treatment employing an aluminum ion source such as alum and a cationic material selected from cationic polymers, starches and gums hereinafter referred to as cationic material for convenience sake. The cationic material and the aluminum ion source may be added together, or separately, in either order. In normal paper mill practice, alum or other aluminum ion sources are most often added to the pulp directly at the beater, and, for this reason, it is preferred that the aluminum ion source be added first. Any aluminum ion source conventionally available to the industry may be employed, such as alum, aluminum chloride, sodium aluminate and the like. For the purposes of this invention, 0.2% to 5% of aluminum ion source, calculated as alum, and based on the dry fiber weight, are used. A preferred range of this additive may be between 0.5% and 1.5%.

The second part of the first component used in the process of this invention is a cationic material defined above as being a material selected from cationic polymers, cationic starches and cationic gums. The amount of the cationic material used is from 0.1% to 3.0%, based on the dry fibre weight. Cationic starches are well known in the papermaking art and have been used for various purposes such as to increase dry strength. Broadly, cationic starches may be defined as any starch which has been modified to impart a cationic character thereto.

The term "starch", as used herein, is intended to mean any of the natural starches, as well as dextrans and the various modified starches and starch derivatives. Examples of natural starches are corn starch, potato, tapioca, waxy maize, rice, wheat and so on. Modified starches and starch derivatives are acid modified, hypochlorite-oxidized and enzyme-converted starches and the acetates and ethers of starch.

While a wide variety of materials may be used to modify starch to impart a cationic character thereto, a preferred class of chemicals which may be satisfactorily employed are polyamines. Normally, polyamines may

be used to impart cationic character to starch by the simple expedient of cooking raw starch in the presence of the polyamine to form a cationic starch solution. A particularly suitable polymeric polyamine which may be used as described herein is defined as being the reaction product of an alkylene dihalide and an amine having the following structural formula:



where R is a bivalent alkyl radical selected from the group of CH_2CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_2$, CH_2

and $\text{CH}_2\text{C}(\text{CH}_3)_2$, and x is an integer of from 0 to 5.

Similarly, cationic gums may be prepared in a like manner for use in the process of this invention. A variety of simple, inexpensive gums may be treated with polymeric polyamines to produce a superior papermaking material upon subsequent treatment of the precursor pulp according to the practice of this invention. Gums susceptible to modification with polyamine materials include, for example, Irish moss, tragacanth, dextrine, Veegum (Registered Trade Mark), carboxymethyl cellulose, locust bean gum, Shiraz gum, Zanzibar gum, karaya gum, agar agar, frankincense, benzoin, gambier, jaguar, psyllium seed, gum arabic, gum acacia, Senegal gum, algin, British gum, flaxseed, ghatti, guar, Iceland moss, quince seed, and other related, readily available gums. Most preferred are guar and locust bean gums.

The gum and polymeric amine when reacted are preferably provided as a relatively dilute aqueous suspension which contains from 1-40% by weight of the reactants and preferably 1-30% by weight. An amount of polymeric amine is present in relation to the gum so as to provide 1-40% of polymeric amine and preferably 1-30% in relation to and based upon the weight of the gum.

Other polyamines which may be used to modify starches and thereby render these materials cationic are: polyethyleneimine, polyethyleneamine, condensation polymers of alkylene polyhalides such as ethylene dichloride and ammonia, or poly nitrogen-containing bases, and addition polymers derived from monomers containing basic nitrogen groups such as dimethylaminoethyl methacrylate, 2-vinyl pyridine or substituted allyl amines. Other materials which may be used to modify starches and gums to impart a cationic character are amines such as 1-trimethylamino-2,3-epoxypropane or 1-dimethylamino-2-chloroethane. One particularly

suitable cationic starch is sold under the trademark "Q-Tac".

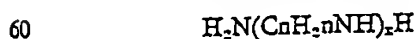
The cationic polymers which may be used in the process of this invention are many and varied. Generally, these polymers have molecular weights in excess of 1000 and more preferably in excess of 2000. The most preferred polymers of this type have molecular weight ranges of 2,000—50,000. Such above polymeric polyamines may be formed by a wide variety of reactions such as by the reaction of alkylene polyamines and difunctional alkyl materials.

A greatly preferred class of polyamine polymers are condensation polymers of alkylene polyamines and halohydrins. Exemplary polymers of this type are those disclosed in Green U.S. Patent 2,969,302, the disclosure of which is incorporated herein by reference.

A preferred polyamine condensation polymer of the type described in Green U.S. Patent 2,969,302, is generically defined as an aqueous solution containing 5—40% by weight of a high molecular weight epihalohydrin-alkylene polyamine condensation copolymer, said aqueous solution being further characterized as having a viscosity of at least 10 cps, when measured as an aqueous solution containing 20% by weight of said condensation copolymer at 75°F. Preferred materials falling within this class have a viscosity of at least 50 cps when measured as just described. The upper limit of the viscosity is anything short of gel formation. Most preferred products have viscosities of from about 50 to about 800 cps. In order to form the preferred polymers of the invention, it is only necessary to polymerize the epihalohydrin and alkylene polyamine at temperatures ranging from about 105°F. to 185°F. at a mole ratio of epihalohydrin to alkylene polyamine falling within the range of 1.4:1 to 2.2:1. For best results, the polymerization reaction is generally carried out in dilute aqueous solutions at reactant concentrations ranging from about 10 to about 30% by weight.

As mentioned above, the two classes of monomeric reactants involved in the condensation polymerization are epihalohydrins and alkylene polyamines. The epihalohydrins that may be employed include such materials as epichlorohydrin, epibromohydrin and epiodohydrin. Of these, the most preferred, due to cost and ready availability, is epichlorohydrin.

The alkylene polyamines which are reacted with the polyfunctional halohydrin for the purpose of the invention are well known compounds having the general formula:



where n is an integer from 1 to 4 and x is one or more. Preferably, n is 2 and x ranges from 1 to 5 to give the preferred polyethylene

polyamine class. Examples of alkylene polyamines useful in the invention are the alkylene diamines, such as ethylenediamine, 1,2-propylene diamine, 1,3 - propylene diamine and the polyalkylene polyamines, such as, for example, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dipropylene triamine, and the similar polypropylene polyamines and polybutylene polyamines. Mixtures of any of the above may also be used and oftentimes commercial sources of these compounds contain two or more of any of the above alkylene polyamines. Some commercial amine products may contain mixtures of as many as five separate compounds.

Yet another species of polyamines falling within the above class is formed by reaction of an alkylene dihalide and an amine. Preferred amine reactants include ammonia, ethylene diamine, diethylene triamine, tetraethylene pentamine and triethylene pentamine. Of these, the most preferable due to excellent reactivity, low cost and availability is ammonia. The alkylene dihalide reactant may be chosen from a wide variety of difunctional organics including ethylene dichloride and 1,2-propylene dichloride. Of these the most preferred is ethylene dichloride. One excellent cationic polymer for use in the instant invention is formed by reaction of ammonia and ethylene dichloride under superatmospheric pressures and with heating.

In addition to the above preferred condensation type polymers, many other condensation polymeric cationics are also admirably suited for use in the invention. Effective watersoluble cationic polymers or resins are to be found among the class consisting of amine-aldehyde resins and amide-aldehyde resins, preferably hydrophilic melamine-formaldehyde resins. Such colloidal cationic resin solutions may be prepared by dissolving ordinary melamine-aldehyde condensation products, such as methylol melamines, in acids such as hydrochloric acid, to form acidified or acid-type resin solutions having a glass electrode pH value within the range of about 0.5 to about 3.5 when measured at 15% solids, or pH values up to 4.5 when measured in more dilute solutions, followed by aging to the colloidal condition, as described in United States Patent 2,345,543.

Another class of cationic melamine-aldehyde resins that may be used in practicing the present invention are the resinous polymers of melamine, urea and aldehydes such as formaldehyde containing at least 0.7 moles of melamine for each 4 moles of urea and about 1 to 4 moles of combined formaldehyde for each mole of melamine plus urea. Such resins are described in U.S. Patent 2,485,079. These cationic melamine resin copolymers are obtained by first preparing an acidified aqueous solution of an aldehyde condensation product

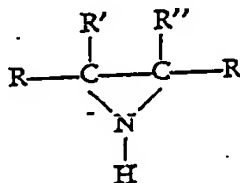
of melamine and urea containing 1 to 70 mole percent of urea and 30—90% of melamine and about 0.2 to 1.5 moles of acid per mole of melamine, depending on the strength of the acid, and aging the solution until the colloidal cationic condition is reached.

Another suitable class of cationic resins are those of the polyimine type. The polyimines are derived, for example, by the homopolymerization of monomers containing the imine radical, $-\dot{N}-$, and have a molecular weight



of at least 1000.

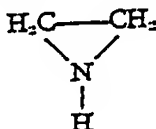
The imine monomers preferably employed contain not more than 7 carbon atoms. Of the monomers employed for making polyimines, some of those best suited for the purpose of the invention are classified as substituted ethylenimines and have the structural formula:



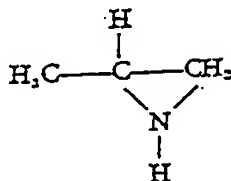
wherein R, R', R'' are either hydrogen or acyclic hydrocarbon radicals containing from 1 to 3 carbon atoms.

Examples of such monomers are the following:

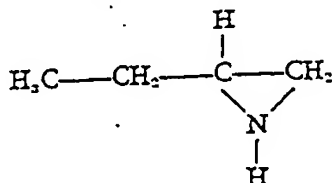
A. Ethyleneimine—



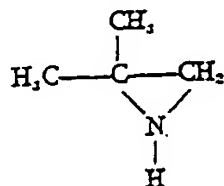
B. 1,2-propyleneimine—



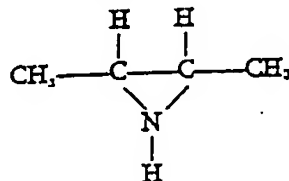
C. 1,2-butyleneimine—



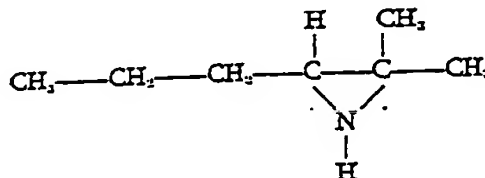
D. 2,2-dimethylethyleneimine—



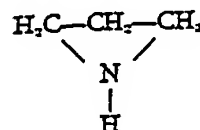
E. 2,3-butyleneimine—



F. 1,1-dimethyl,2-n-propyl-ethyleneimine—



Other monomers capable of producing cationic polymers suitable for the practice of this invention are trimethyleneimine which has the structural formula:



and its lower alkyl substituted derivatives in which one or more of the hydrogen atoms attached to a carbon atom is substituted by an alkyl group containing not more than 3 carbon atoms, i.e., methyl, ethyl and propyl.

Ethyleneimine, as well as many of its derivatives, may be prepared by any of several well known methods such as are described in the "Journal of American Chemical Society", Vol. 57, p. 2328, (1935) and Ber. 21 1094 (1883).

The polymerization of ethyleneimine and its derivatives is usually conducted at reduced temperatures using acid catalysts such as HCl and the like. The polymerization of the various monomers listed above is described in detail in the "Journal of Organic Chemistry", Vol. 9, p. 500, (1944).

The linear polyimines are characterized by a long acyclic chain structure in which nitrogen atoms of imine groups are connected at intervals to carbon atoms. It will be recognized, therefore, that linear polyimines can be

prepared not only by homopolymerization but also by condensation reactions with the elimination of a hydrohalide. Thus, ethylene dibromide or propylene dibromide can be condensed with diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and/or dipropylenetriamine to produce polyimines, and the present invention contemplates the employment of such materials.

In general, the polyimines employed in the practice of the invention can be described as water-soluble polyimines in which imino (=NH) groups are attached to carbon atoms and recur every two to three atoms in a main linear chain, preferably containing not more than 6 carbon atoms in any side chain. Where imino groups are separated from each other by ethylene groups, the linear polyimines are referred to as polyethyleneimines. Where the imino groups are separated from each other by propylene groups, the linear polyimines are referred to as polypropyleneimines.

The molecular weight of the useful imine polymers should be at least 1,000 and is preferably from 5,000 to 50,000. If the condensation reactions from which these polymers are derived are allowed to continue for too long a period of time or the conditions are not suitable, infusible, water-insoluble resins may result. In the case of 2,2-dimethylethylenimine, care must be used to control the reaction so that the materials produced are sufficiently water-soluble so that they can be employed at effective concentrations. Similarly, long chain water-soluble cationic polymers may be prepared by condensing formaldehyde with a polyalkylene polyamine such as tetraethylenepentamine to link the polyamines with a plurality of methylene bridges.

The above type condensation polymers may be generally described as water-soluble cationic polymers containing a plurality of cationic sites in a straight or branched chain configuration.

Yet another class of cationic resins include addition-type polymers which in aqueous medium will form organic cations having a substantial number of positive charges distributed at a plurality of positions on the polymer. Generally, these materials have a molecular weight in excess of 100,000 and contain in a side chain a hydrophilic group possessing the ability to form the above described positive charge. Typical members of this group are polyvinyl pyridine or other similar monomers having nitrogen-containing nuclei. Another specific material of this type is polyvinyl pyrrolidone. Salts of the above may also be employed.

Still other suitable cationics include the well known vinyl benzyl quaternary ammonium compounds such as the homopolymers of vinyl benzyl quaternary ammonium salts or copolymers thereof formed by a copolymerization reaction with acrylamide, methacrylamide, etc.

The vinyl benzyl quaternary materials are generally formed by chloromethylating polystyrene and subsequently substituting the chloro group with a tertiary amine to produce the corresponding nitrogen quaternary.

Other examples of cationic polymers suitable as a treating agent in the first step of the process of the invention includes homopolymers and water-soluble copolymers of aminoethyl acrylate hydrochloride, aminoethyl methacrylate hydrochloride, or substituted ammonium alkyl acrylates or methacrylates such as N-methyl or N,N-dimethyl-amino-alkyl acrylate or methacrylate wherein the alkyl groups contain 2-3 carbons. Other cationic polymers may be formed when the cationic monomer of the type just described is copolymerized with any one or more monoethylenically unsaturated monomers capable of vinyl polymerization such that the resulting copolymer is water-soluble or water-dispersible. Suitable monomers of this type which may be copolymerized with the cationic monomers include acrylamide, methacrylamide, acrylonitrile, the lower (i.e. containing no more than 6 carbon atoms) alkyl esters of acrylic and methacrylic acid, or vinyl methyl ether.

Preferred cationic materials for use in the process include (1) cationic starches of the type described above and of the type sold under the trademark Q-Tac, and (2) a cationic copolymer of dimethylaminoethyl methacrylate and acrylamide. The following materials can be used in preparing the polymer:

Acrylamide	— 101.25 g.	100
Dimethylaminoethyl Methacrylate	— 33.75 g.	
HCl (Cp Grade 37-38%)	— 21.00 g.	
H ₂ O (distill)	— 144.00 g.	
Total 300.00 g.		

The dimethylaminoethyl methacrylate is dissolved in 144 g. of distilled water and the solution is cooled to 25°C. Enough hydrochloric acid is slowly added to the solution with adequate mixing to lower the pH to 5.0 while maintaining the 25°C. temperature during neutralization. The acrylamide (101.25 g.) is added to the reaction mixture until it dissolves. The total monomer solution is then readjusted to pH 5.0.

A quantity of 2.7 g. petroleum sulfonate is dissolved in 592 g. of toluene and charged to the reaction vessel. The toluene mixture is heated to 50°C. and purged with nitrogen at a rate of 1500 cc./min.

A quantity of 0.166% tertiary butyl hydroperoxide 70, based on 135 g. of monomer, was added to the total monomer solution with stirring. This monomer solution was then added to the heated toluene mixture and the temperature was maintained at 50°C. with nitrogen purging. This reaction mixture is then maintained at 50°C. for 2 hours after

initiation. After the 2 hour reaction, the water was removed by azeotropic distillation and the polymer was isolated from the toluene and air dried.

5 The polymer that is produced by the above procedure has a viscosity of about 3000 cps. It is a water-soluble dimethylaminoethyl methacrylate-acrylamide copolymer. The procedure can, of course, be widely varied. One
10 per cent (1%) solution viscosities can be as low as 100 cps and range up to 5000 cps. Our preferred product has a viscosity in the range of 2000—4000 cps. A 1% solution viscosity of about 3000 to 4000 cps represents a
15 molecular weight of about 2—3 million. The amine to acrylamide ratio can be varied easily from 5%, to 50% by weight. Other acids can, of course, be used for neutralization and other emulsifiers can be substituted for the petroleum
20 sulfonate. Other solvents, including aromatic, aliphatic or chlorinated solvents, can be substituted for the toluene. Any organic peroxide or inorganic redox system will work in the process.

25 The amount of the cationic colloid may conveniently range from 0.1% to 3.0% based on the dry fiber weight. A preferred range of this additive is from 0.2% to 1.5%.

30 The second component used in this invention may be broadly defined as being an anionic high molecular weight polymer.

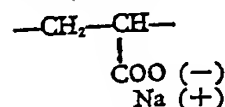
Polymers falling within the above definition are those consisting of substances which in an aqueous medium will form organic anions having a measurable negative electric charge. Greatly preferred anionic materials are those substances polymeric in nature having a substantial number of negative electrical charges distributed at a plurality of positions on the polymer. These polymeric anionic substances which have a molecular weight of at least 100,000 are derived by polymerization of at least one mono-olefinic compound through an aliphatic unsaturated group. These polymers should be water-soluble or dispersible and have a structure substantially free of cross linkage and are therefore available for solubilization or dispersion in water. Preferred anionic substances found to be especially effective for the purpose of the invention are water-dispersible synthetic polymers having a linear hydrocarbon structure and containing in a side chain a hydrophilic group consisting of carboxylic acid, carboxylic acid anhydride, carboxylic acid salt groups, or copolymers of any of the foregoing. Typical water-dispersible synthetic organic polymers, anionic in nature, which have these characteristic groupings are listed below. These have been found to be effective for the practice of the invention.

No.

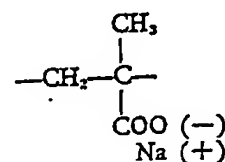
Name

1 Polyacrylate-sodium salt

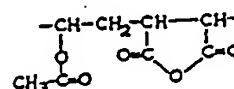
Characteristic Grouping



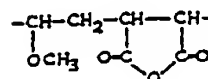
2 Polymethacrylic acid-sodium salt



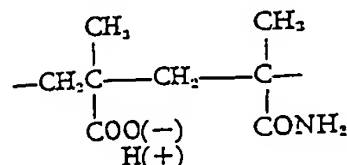
65 3 Maleic anhydride-vinyl acetate copolymer



4 Polyvinyl methyl ethermaleic anhydride copolymer



5 Methacrylic acid-acrylamide copolymer



No.	Name	Characteristic Grouping
6	Polyacrylic acid	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{COO}(-) \\ \text{H}(+) \end{array}$
7	Isopropenyl acetate - maleic anhydride sodium salt	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---CH---CH---} \\ \quad \quad \\ \text{O} \quad \text{C=O} \quad \text{C=O} \\ \quad \quad \\ \text{CH}_3\text{C=O} \quad \text{O}(-) \quad \text{O}(-) \\ \quad \quad \text{Na}(+) \quad \text{Na}(+) \end{array}$
8	Itaconic acid-vinyl acetate	$\begin{array}{c} \text{COO}(-)\text{H}(+) \\ \\ \text{---CH---CH}_2\text{---CH}_2\text{---CH---} \\ \quad \\ \text{CH}_2\text{COO}(-) \quad \text{O} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_3\text{C=O} \end{array}$
9	α - methyl styrene - maleic anhydride sodium salt	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---CH}_2\text{---CH---CH---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{COO}(-) \quad \text{COO}(-) \\ \quad \quad \text{Na}(+) \quad \text{Na}(+) \end{array}$
10	Styrene-maleic anhydride sodium salt	$\begin{array}{c} \text{---CH---CH}_2\text{---CH---CH---} \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{COO}(-) \quad \text{COO}(-) \\ \quad \quad \text{Na}(+) \quad \text{Na}(+) \end{array}$
11	Methylmethacrylate - maleic anhydride salt	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---CH}_2\text{---CH---CH---} \\ \quad \quad \\ \text{COOCH}_3 \quad \text{COO}(-) \quad \text{COO}(-) \\ \quad \quad \text{Na}(+) \quad \text{Na}(+) \end{array}$
12	Acrylic acid-styrene copolymer	$\begin{array}{c} \text{---CH---CH}_2\text{---CH---CH}_2\text{---} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{COO}(-) \\ \quad \quad \text{H}(+) \end{array}$

10 A suitable anionic copolymer may be derived from a polycarboxylic acid monomer and at least one other monomer copolymerizable therewith. The polycarboxylic acid may be maleic anhydride, acrylic acid, maleic acid, fumaric acid, itaconic acid, aconitic acid or citraconic acid, which may be copolymerized with the amides of these acids, the alkali metal derivatives (e.g., sodium, potassium and lithium), the alkaline earth metal derivatives (e.g., magnesium, calcium, barium and strontium), and ammonium salts of these acids, the partial alkyl esters (e.g., methyl, ethyl, propyl, butyl, mono esters),

the salts of said partial alkyl esters, and the substituted amides of these polycarboxylic acids. Where a hydrophilic polycarboxylic acid such as maleic acid is used as one of the starting components to form the copolymer, a hydrophobic comonomer may be used, as for example, styrene, α -methylstyrene, vinyl toluene, chlorostyrene, vinyl acetate, vinyl chloride, vinyl formate, vinyl alkyl ethers, alkyl acrylates, alkyl methacrylates, ethylene, propylene, and/or isobutylene. The foregoing synthetic copolymers are preferably obtained by reacting equimolar proportions of a polycarboxylic acid and at least

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one other monomer. However, certain of the unsaturated polycarboxylic acids can be polymerized in less than equimolar proportions with some of the less hydrophobic comonomers.

Another preferred class of anionic polymers is a linear high molecular weight polymer or copolymer of a vinyl aryl hydrocarbon, such as styrene, vinyl toluene, alpha-methylstyrene and vinyl xylene, which are polymerized, and then sulfonated under controlled conditions to produce a water-soluble substantially linear polymer sulfonate.

Another class of anionic materials particularly suitable in the practice of the invention are defined as anionic acrylamide polymers, preferably having a molecular weight of at least 250,000, exemplified by copolymers of sodium acrylate and acrylamide. The most preferred copolymers of this type may be termed acrylamide polymers and comprise 5—95% by weight of sodium polyacrylate and 5—95% by weight of polyacrylamide and have a molecular weight in excess of one million. Other polymers or copolymers of acrylic acid types are particularly preferred and are typified by those obtained by vinyl polymerization of acrylic acid, methacrylic acid, sulfoethyl acrylate, carboxyethyl acrylate or salts thereof or copolymers thereof of the acids or salts obtained by suitable copolymerization with monomers such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, lower alkyl esters of methacrylic acid, alkyl esters of the acrylic acids and vinyl alkyl ethers. The inclusion of a third monomer in amounts ranging up to 20% are by weight also provides polymers which are effective.

The above described anionic polymers may be prepared by well known techniques. A number of the above polymers are available commercially in substantial quantities.

The preferred anionic polymers for use in the process are terpolymers made from three groups of monomers. The monomers are polymerized in the presence of each other in a single step process to give a terpolymer with the type and amount of recurring units and their respective polar groupings being dependent upon the amount of each monomer employed. The exact molecular configuration, of course, cannot be determined, but is rather considered a statistical average according to the ratio of the monomers employed one to the other with their respective side-groups. Extremely high molecular weights of 5,000,000 or more and the desired physical characteristic of free-flowing white powder are obtained through a special polymerization technique which will be discussed in more detail hereinafter.

The first essential monomeric starting reactant is acrylamide. This monomer is easily

obtained by well known commercial processes such as partial hydrolysis of acrylonitrile. It has been determined that the amount of acrylamide which shall be employed to give desired drainage results is 85—95 parts by weight. The most preferred range of acrylamide used is 89.5 to 94.5 parts by weight.

The next monomeric starting material is a polymerizable polycarboxylic acid which may be chosen from maleic acid, maleic anhydride, or fumaric acid. Again, the amounts of starting polycarboxylic acid monomer used is important. Excellent retention activity is achieved when from 0.3 to 2.0 parts by weight of the above compounds such as maleic anhydride is employed. The most preferred retention aids comprise those including from 0.5 to 1.5 parts by weight of the polycarboxylic acid monomer. Due to low cost and availability, the most preferred of the above three materials is maleic anhydride which during the polymerization reaction both hydrolyzes and polymerizes to form a plurality of carboxylic acid groups.

The last monomeric reactant is a water-soluble ethylenically unsaturated monomer containing polar groups; examples of such monomers are acrylic acid and salts and alkyl esters thereof, vinyl pyrrolidone, vinyl acetate, methacrylamide, vinyl alkyl ethers such as methyl vinyl ether, methacrylic acid and salts and alkyl esters thereof, acrylonitrile, methacrylonitrile, allyl alcohol and allyl amine. By use of the term water-soluble it is intended to include not only those substances which are soluble in all proportions with water, but also to include monomers which may have low solubility, but nevertheless may be dispersed or emulsified in water by suitable techniques. The amount of ethylenically unsaturated monomer employed as a starting material should vary from about three to about fifteen parts by weight. Best results with regard to retention activity and desired physical characteristic of free-flowing powder is reached when from five to nine parts by weight of ethylenically unsaturated monomer is employed.

The terpolymers of the invention then, include the following polymeric reactants and their range of starting material weights.

Composition A	
Monomer	Parts by Weight
Acrylamide	85.0—95.0
Polycarboxylic acid monomer	0.3— 2.0
Ethylenically unsaturated water-soluble monomer	3.0—15.0

Composition B shows the more preferred general terpolymers of the invention and their respective weight ranges.

Composition B		
Monomer	Parts by Weight	
Acrylamide	89.5—94.5	
Polycarboxylic acid monomer	0.5—1.5	
5 Ethylenically unsaturated water-soluble monomer	5.0—9.0	

The most preferred specific terpolymer of the invention having the range of reactant weights as outlined in Composition B above includes polyacrylamide, maleic anhydride 10 and methacrylic acid.

In order to produce terpolymers of exceedingly high molecular weight, and correspondingly proportional excellent retention ability, a special polymerization technique was employed. Broadly speaking, this technique involved preparation of the highly concentrated monomer solution, addition of an inert heat transfer solvent media, which may be referred to as an organic solvent, and subsequent polymerization effected at relatively low temperatures. The polymerization must be carried out under conditions of high agitation and in the presence of an antisticking agent, which acts to keep the formed polymer from agglomerating into an impractical and unusable mass. If conditions are followed closely, granules of relatively small size may be obtained which are easily ground into a freeflowing white soluble powder, and are immediately ready for use without further processing. The monomers actually terpolymerize in a separate stratum within the above system in the presence of a surface active compound acting as the anti-sticking agent. 35

More specifically, an aqueous solution is prepared containing about 30% to about 80%, by weight of monomers, 20% to 70% water, and 0.003% to about 0.2% based on the weight of monomer present of a polymerization catalyst, such as potassium persulfate. The water solution is then added to or mixed with a water-insoluble, organic, heat transfer medium which preferably is capable of forming an azeotropic mixture with water. The above mixture should contain a minor amount of a surface active agent which prevents the terpolymer from sticking to the agitator or the walls of the vessel. The temperature of the system is raised to a desired point and the mixture is kept in motion by means of an agitator. Oxygen is removed from the system either by purging with an inert gas such as nitrogen or carbon dioxide, 55 by applying a vacuum or by boiling the mixture. The polymerization is initiated as soon as the oxygen is removed. If an emulsion is formed due to the presence of the surface active agent, the emulsion breaks and the polymerization is carried out in a separate layer. The organic heat transfer medium substantially surrounds the aqueous medium as the polymerization takes place. Vigorous agitation is employed to continuously shear

the polymer layer into particles which vary 65 in diameter, for example, from about 1/16" to about 2" and more often from about 1/4" to 1/2". In a preferred process, the temperature of the mixture is raised to its boiling point or maintained at the boiling point in the event polymerization was carried out at the boiling point of the mixture and after the polymerization is completed, water is removed by azeotropic distillation. The boiling temperature, of course, varies in accordance with the particular organic heat transfer agent in the mixture. 70 75

During the boiling off stage, the organic solvent preferably is condensed and returned to the mixture while the water is being trapped and removed. After from 60 to 100% of the water has been eliminated the granules that have formed are separated from the solvent by filtration and are then washed and air dried. 80 85

It has been found that benzene, toluene, xylene, and ethylene dichloride are especially suitable for use in the present process as well as carbon tetrachloride and tetrachloroethylene. Other comparable organic compounds that form azeotropic mixtures of water, however, could be used without difficulty as long as they do not contain alcohol, aldehyde or ketone groups which would cause undesirable side reactions. The polymerization medium can also contain a nonazeotropic component with boiling point above the distilling temperature. The above materials may be termed organic solvents and are all water insoluble, organic heat exchange materials which are considered inert in the practice of the invention. These organic substances serve as heat transfer media or heat dissipators by suspension of the aqueous monomer phase and subsequently form terpolymeric product. 90 95 100 105

The catalysts that are employed in the process include conventional peroxidic oxidizing agents such as potassium persulfate, hydrogen peroxide, and ammonium persulfate. It is preferred that water-soluble compounds be used for this purpose. The amount of catalyst used in the process can vary from 0.003% to about 0.2% by weight based on the weight of the monomers. A preferred range is from about 0.003% to about 0.05%. Catalyst concentrations above 0.2% will polymerize the aqueous solution containing the three monomers, but the resultant products are inferior to those prepared using amounts of catalyst within the specified ranges. One of the advantages of the subject process, therefore, is that it provides a means of carrying out the polymerization using very small amounts of catalyst. 110 115 120

As was pointed out above, a surface active agent should be added to the polymerization mixture in order to prevent the polymer from sticking to the walls of the reaction vessel and to the agitator. There are numerous 125

compounds on the market which would perform satisfactorily in the capacity. Materials such as "Ethomid" S-15, O-15, and HT-15, which are ethylene oxide condensates of fatty acid amides, as well as "Arlacel 80" and "Span 80", which are sorbitan mono-oleates, will serve adequately as antisticking agents as will sorbitan mono-stearate, sodium dodecyl benzene sulfonate, aluminum stearates, and aluminum oleates. ETHOMID, ARLACEL and SPAN are Registered Trade Marks. Initially in the process, the presence of the surface active agent may cause the formation of an emulsion. It is essential, however, that the emulsion break and form two separate and distinct layers prior to the polymerization reaction. The amount of surface active agent which is added to the system can vary from about 0.5% to about 7% by weight based on the weight of the heat transfer medium, and preferably will vary from about 2% to about 4% by weight. During the polymerization, the monomer-containing aqueous medium is substantially surrounded by the organic heat transfer medium.

In a preferred embodiment, the polymerization reaction is carried out using a redox type catalytic system. In the method described above, either avoiding or removal of oxygen by other means is needed to permit the catalyst to form free radicals. In a redox system, the catalyst is activated by means of a reducing agent, which in the absence of oxygen immediately produces free radicals without the use of heat. One of the reducing agents most commonly used is sodium metabisulfite. Other suitable agents include water-soluble thiosulfates, bisulfites, hydrosulfites, and reducing salts, such as the sulfates of metals which are capable of existing in more than one valence state. The metals include cobalt, iron, nickel, and copper. The use of a redox initiator system has several advantages, the most important of which is that it is possible to carry out the polymerization at lower temperatures. It is not required to decompose the catalyst.

As has been pointed out, a great many surface active agents can be used in the terpolymerization process. Those compounds mentioned above are illustrative of suitable and readily available products. The amount of surface active agent used in the process can vary from about 5 to 7%, and preferably 2% to 4% by weight based on the weight of the heat transfer medium. Too large a quantity of the surface active agent should be avoided inasmuch as an excess might tend to form stable emulsions or suspensions. The surface active agents function primarily to prevent the forming terpolymer from sticking to either the agitator or walls of the reaction vessel.

The selection of particular catalysts—or activators, should a redox system be em-

ployed—for use in the process does not fall within the scope of our invention. Conventional catalysts such as potassium persulfate, and conventional activators, such as sodium metabisulfite, work very satisfactorily. It is important, however, that the amount of catalyst used in the process vary from 0.003% to about 0.2%, based on the weight of the monomers.

It is preferred to dissolve the catalyst and the activator in separate water solutions prior to adding to the aqueous solutions of the three monomers. The catalyst and activator can be dissolved in the aqueous monomer solution just prior to adding the solution to the organic heat transfer agent. Alternatively, the catalyst can be dissolved in a small amount of water and then be added to the organic heat transfer medium prior to the addition of the monomeric solution. Another satisfactory method would be to dissolve the catalyst and/or activator in water and add this solution to the reaction mixture after the monomeric solution has been added to the heat transfer medium.

The water content of the terpolymers that are produced by the above method should range from 0 to about 28%. Our preferred water content range is from about 5% to about 15%. If the moisture content of the polymer is greater than about 28%, the granules tend to agglomerate.

Several organic relatively water-insoluble heat transfer liquids have been suggested above which can be used in the subject process. It is preferred that those liquids form azeotropic mixtures with water. By azeotropic mixtures, we mean mixtures which on heating will cause water to distil over at temperatures below the normal boiling of the water at a given pressure. The use of an azeotropic mixture makes it possible to remove water from the terpolymer particles without employing special drying equipment. Apart from the fact that these liquids must not contain reactive groups such as alcohol, aldehyde, and ketone groups, which would cause side reactions, the selection of the particular heat transfer medium is not particularly critical. Benzene is a relatively inexpensive component and it has been found to provide excellent results. For this reason, it is our preferred heat transfer material.

As was pointed out above, the heat transfer medium plays an important part in the concentrated solution polymerization method. In particular, the function of the organic liquid is to remove the heat of reaction from the forming polymer.

One of the important steps of the polymerization process involves the removal of dissolved oxygen gas from the reaction mixture. The removal of the oxygen can be accomplished by (1) purging the reaction mixture with an inert gas such as nitrogen

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or carbon dioxide, (2) boiling the reaction mixture, and (3) applying a partial vacuum to the system. If an inert gas is used to remove the oxygen, it is best applied by passing the gas through a disperser or sparger which is inserted beneath the surface of the reaction mixture.

One of the major disadvantages of the prior art methods is that only dilute solutions of monomers could be polymerized without causing a violent reaction or without producing a rubbery, nonflowable material. In the subject process, the total monomer content of the aqueous solution can range from about 30% to about 80% by weight. Primarily because it is possible to work with concentrated solutions of monomer, the formed terpolymers have unusual and highly advantageous properties.

The following examples illustrate typical terpolymers and their method of preparation.

EXAMPLE 1

This example illustrates a typical terpolymer involving terpolymerization of maleic anhydride, methacrylic acid and acrylamide using a redox system of polymerization and a high concentration of monomers via the polymerization technique as described above. Unless otherwise indicated, the percentage figures below are to be taken as percent by weight.

To 108.0 grams of water (12.6%) are added 1.125 grams of maleic anhydride (0.13%), 9.4 grams of methacrylic acid (1.11%), and 10.0 grams of a 50% concentrated aqueous solution of sodium hydroxide (1.17%). The above ingredients are mixed until complete solubilization is effected. 124.425 grams of acrylamide (14.59%) are added to the above mixture and the entire solution was gently agitated and mildly heated at a temperature not greater than 38°C. It is essential that the temperature not exceed above this figure since heating at a higher temperature would effect polymerization prematurely. The pH of the solution is then adjusted with 50% caustic sufficient to raise the pH to 9.0.

In a separate 1000 ml three-necked flask, equipped with thermometer, Dean and Stark trap, condenser, stirring device and heating mantle attached to a variable transformer are added 754.0 grams of toluene (67.32%) and 19.6 grams of "Arlacel 80" antisticking agent (2.30%). The reaction flask then is purged with nitrogen at a rate of 960 cc/min. After the inert solvent and antisticking agent mixture is purged sufficiently, the above basic monomeric solution is added to the 1000 cc reaction flask. The system is put under reduced vacuum (8 inches) and heated to 70°C. After this temperature is reached, the vacuum is shut off and 4.8 grams of a 1% aqueous solution of $\text{Na}_2\text{S}_2\text{O}_4$ is added (0.56%) while

the stirring mechanism is running. After a few seconds, 1.2 grams of a 1% aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ (0.14%) is added. During this addition of redox reagent, the reaction temperature drops two to three degrees C. The redox catalyst is completely added, the vacuum is re-established at an 8" reading, and the reaction mass reheated to 70°C. When this temperature is again reached the vacuum is shut off and only nitrogen is introduced into the reaction mixture for the duration of the reaction time. Heating is applied in order to maintain the reaction mass at 70°C. until an exotherm occurs. At this time, heat is discontinued and the temperature drops of its own accord to 68°C. After the exothermic reaction has been completed, temperature of the mixture of the polymerization reaction is maintained at about 70°C. for 50-60 minutes. At this time, water is then removed as an azeotropic distillate. Approximately 90% of the total water added was azeotroped off. Filtration from the organic solvent left a white granular product.

EXAMPLE 2

This example was run similar to the procedure outlined in Example 1. To a 500 ml beaker were added 85.5 grams acrylamide, 4.0 grams of methacrylic acid, 0.5 grams of maleic anhydride, and 72 mls of distilled water. The monomeric solution was stirred and the pH was adjusted from 3.2 to 6.3 with 50% concentrated sodium hydroxide. With gentle stirring 0.8 mls of a 1% aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ and 3.2 mls of a 1% aqueous solution of $\text{Na}_2\text{S}_2\text{O}_4$ were added to the above monomeric solution. In a separate 1000 ml reaction flask the inert organic solution containing the heat transfer media and anti-sticking agent were prepared. This solvent solution contained 574 grams of toluene and 19.6 grams of Arlacel 80. After heating the inert solvent solution to 71°C. with stirring, the monomeric aqueous solution was added slowly to the reaction flask. The temperature during the addition then dropped to 55°C. whereupon the entire mixture was reheated to 75°C. At this time, a 8" vacuum was applied and a nitrogen layer was put over the reaction surface. The temperature was maintained at 75°C. for 26 minutes, after which time a phase separation was noted. During this time, a vacuum was continuously applied and nitrogen flowed over the surface. After the temperature had dropped about 74°C. the polymerization was considered complete and then the water was removed by azeotropic distillation. 72 mls of water was removed by this method. The resultant white free-flowing granules were washed and separated by vacuum filtration. These granules could be easily ground to below 40 mesh.

The amount of anionic polymer which should be added to carry out the process of this invention will vary depending upon the amount of cationic colloid. A preferred range for this additive may be expressed by a weight ratio of colloid to anionic polymer of about 25:1 to about 1:2. Most preferred is to employ sufficient polymer to have a weight ratio, as above, of from 15:1 to 1:1.

As stated above, the process of this invention comprises adding to an aqueous suspension of paper pulp fibers in sequential order, a cationic component comprising an aluminum ion source and a material selected from cationic polymers, cationic starch and cationic gum, followed by an anionic polymer as defined above. Thereafter, the treated pulp suspension may be formed into paper by any of the conventional papermaking devices in which the aqueous portion of the suspension is drained from the fibers leaving a fibrous web which is thereafter dried into paper. The aluminum ion source and the cationic material can be added at the same or different times. It is preferred, however, that the aluminum ion source be added first followed by the cationic material. In all cases the anionic polymer is added after the aluminum ion source and the cationic material.

The alum, as mentioned above, is preferably added to the pulp suspension at the beater in accordance with normal paper mill practice. However, any other suitable point of addition, such as immediately prior to the fan pump, is acceptable. Also, the cationic material may be added at any point in the papermaking process prior to the point at which the suspension is spread onto the Fourdrinier wire or other foraminous device. Once these two materials, which make up the cationic component, have had sufficient time to be reasonably well distributed throughout the pulp suspension, the anionic polymer may be added. A preferred practice is to add the anionic polymer to the pulp suspension just prior to the headbox. Sufficient time is thereby allowed to uniformly distribute the anionic polymer and thereby achieve maximum benefits from the treatment without materially altering the characteristics of the pulp suspension prior to its formation into a fibrous web. The following examples are presented to illustrate various embodiments of the invention.

EXAMPLE 3

In this example, the process of this invention was employed in a large paper mill located in the Northwestern portion of the United States. The paper being produced was a liner-board grade of paper having a basis weight of approximately 54 lbs. per 1000 ft.². Prior to the addition of any

chemicals, the paper machine was adjusted to run at a maximum rate.

The governing factor which controlled the production rate was the amount of time which was necessary to drain the aqueous portion from the fibers and form what is known as a wet web. A phenomenon was observed which is known as the wet-line, a term used in the papermaking art to indicate that point on the Fourdrinier wire at which the aqueous suspension of pulp fibers actually forms into a cohesive web of fibers. Once the paper machine had achieved equilibrium, various chemicals were added to the aqueous suspension to determine their effect upon this stabilized wet-line. No effect was noticed by mill personnel when approximately 2% alum, based on the fibers, was added at the beater. Next, just prior to the fan pump, 15 lbs. of a cationic starch per ton of dry fibers was added. The particular cationic starch employed in this experiment was a starch ether which was etherified with a reaction product of epichlorohydrin and trimethylamine in contact with a strongly alkaline catalyst. At this point, only slight variation in the wet-line was noticed, with the wet-line moving almost imperceptibly toward the headbox indicating very slight improvement in the drainage rate.

Following this step, an anionic polymer prepared from a mixture of monomers comprising approximately 85% acrylamide and 15% acrylic acid and having a molecular weight in excess of 100,000 was added just prior to the headbox. Almost immediately after the polymer addition, dramatic effect upon the wet-line was noticed, with substantial improvement in the rate of drainage. Specifically, the wet-line was observed to migrate toward the headbox at a noticeable rate. Once equilibrium of the system had again been established, it was determined by mill personnel that approximately 25% improvement in drainage had been effected as evidenced by wet-line migration.

In order to determine the resulting saving realized by this particular paper mill, using the process described above, the rate of production was increased until the wet-line had returned to its original position. Once the system was again stabilized, this particular paper machine was able to produce over 20% more paper per hour, thereby demonstrating the commercial effectiveness of the process of this invention.

EXAMPLE 4

In this example, a number of experiments were performed on unbleached softwood kraft pulp to determine the various effects on drainage of the process of this invention. The apparatus in which the drainage was evaluated consisted of a cylinder having a

screen and a vacuum device mounted on the bottom thereof. Drainage was measured by adding a known quantity of an aqueous suspension of paper pulp fibers to the device and measuring the amount of time required to drain the aqueous portion of the suspension from the fibers under a constant vacuum suction. Prior to any refining, the particular pulp used in these experiments had a drainage rate of 6 seconds. Paper produced from this unbeaten stock was wholly unacceptable for any commercial paper application. The pulp was then beaten to sufficient stock consistency to allow the sample to drain in 100 seconds. Although this beaten pulp possessed superior dry strength and the quality of the paper produced from this pulp was rated acceptable, the drainage rate was too slow for efficient production of paper. Ideally, the optimum situation would be where a pulp would possess the drainage properties of unbeaten pulp and would have the strength and other qualities of the heavily beaten stock. Accordingly, pulps were prepared according to the process of this invention in order to achieve that desired end result.

A series of drainage evaluations were made to demonstrate the surprising effectiveness of the particular steps of the process of this invention. Specifically, Run A represents the above mentioned unbeaten stock with no additives. Likewise, Run B was the above mentioned beaten stock with no additives. Run C comprises beaten stock to which had been added 1.5% of a cationic starch. Run D also contained 2% alum plus 1.5% cationic starch. Run E represents a run using 0.2% of a cationic polymer, in this case a polyamine derived from condensation of epichlorohydrin and an alkylene polyamine. Similarly, Run F represents the use of 2% alum plus 0.2% of the same cationic polyamine as additives. Run G contained 2% alum and 0.1% of an acrylamideacrylic acid copolymer having a molecular weight of approximately 4 million. Run H contained 1.5% cationic starch and 0.1% of the above mentioned anionic polymer. Run I represents the use of the cationic polyamine at a dosage of 0.2% plus 0.1% of the anionic polymer mentioned above. Run J, which represents the process of this invention, was made with a pulp containing 0.5% of alum plus 0.5% of the cationic starch and 0.1% of the above mentioned anionic polymer. Likewise, Run K was run according to the process of this invention using 1% alum plus 1% cationic starch plus 0.2% of the anionic polymer. Finally, Run L, again according to the process of this invention, contained 0.5% alum, 0.15% of the cationic polyamine and 0.1% of the anionic polymer. All of the percentages above are based on the bone dry weight of the fibers. In each case, the first named additive was added first. The results of

these runs are presented below in the following table.

Run No.	Drainage Time, Seconds	
A	6	
B	100	
C	99	
D	96	
E	97	
F	76	75
G	54	
H	84	
I	91	
J	18	
K	8	80
L	14	

As can be seen from Table I above, only Runs J, K and L showed a substantial reduction in drainage rate. In fact, the heavily beaten pulp employed in Run K was modified by the process of this invention to such an extent that it approached the freeness (drainage properties) of unrefined pulp as in Run A. Runs C, D, E, F, G, H, and I represent processes wherein only two of the three required additives were employed. In comparison to the process of this invention, none of these runs were able to effect substantial reduction in drainage rates.

Similar experiments performed on other pulps using other cationic polymers, cationic starches and cationic gums in conjunction with alum, aluminum chloride and sodium aluminate as well as a wide variety of anionic polymers having molecular weights ranging from as low as 100,000 to as high as 5 million. In each case, similar substantial improvements in drainage were noted. Also, experiments were performed to determine the quality of the paper produced under the process conditions. In numerous cases, strength, fold resistance and many other properties were superior to properties of papers produced from heavily beaten unmodified pulps.

As was pointed out above, in our process the combination of materials includes either (1) alum-Q-Tac-anionic polymer (acrylamide plus polycarboxylic acid monomers plus ethylenically unsaturated water-soluble monomer), or (2) alumcationic polymer of dimethylaminoethyl methacrylate and acrylamide-anionic terpolymer. Either of these combinations provides a much improved drainage rate while maintaining paper strength, etc.

WHAT WE CLAIM IS:—

1. A process for making paper from an aqueous suspension of paper pulp fibres, which comprises: treating said suspension sequentially with (a) a cationic component

- comprising from 0.2% to 5.0% of an aluminum ion source, calculated as alum, and based on the dry fibre weight, and from 0.1% to 3.0% of a material selected from
- 5 a cationic polymer, a cationic starch and a cationic gum, based on the dry fibre weight of said suspension, and (b) an anionic polymer having a molecular weight of at least 100,000 in an amount sufficient to provide
 - 10 a weight ratio of said material to said anionic polymer of from 25:1 to 1:2, thereby forming a treated pulp suspension; and thereafter forming said treated suspension into a fibrous web by means of a foraminous device which
 - 15 drains the aqueous portion of said suspension from said fibres.
 2. A process according to claim 1, in which said aluminum ion source is added to said suspension prior to said cationic material.
 - 20 3. A process according to claim 1 or claim 2, in which said aluminum ion source is added in an amount of from 0.5% to 1.5%.
 4. A process according to any one of claims 1, 2 and 3, in which said cationic material
 - 25 is added in an amount of from 0.2% to 1.5%.
 5. A process according to claim 4, in which said weight ratio is from 15:1 to 1:1.

6. A process according to any one of claims 1 to 5, in which said anionic polymer is an anionic acrylamide polymer having a molecular weight of at least 250,000.

7. A process according to any one of claims 1 to 6, in which said cationic material is a cationic starch or a cationic copolymer of dimethylaminoethyl methacrylate and acrylamide.

8. A process according to claim 7, in which said anionic polymer is a terpolymer produced by copolymerising the following monomers:

Monomer	Parts by Weight	
Acrylamide	85.0—95.0	
Polycarboxylic Acid Monomer	0.3—2.0	
Other Ethylenically Unsaturated Water-soluble Monomer	3.0—15.0	45

9. A process according to claim 1, substantially as hereinbefore described.

10. Paper when prepared by a process according to any one of the preceding claims.

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